

1915
W587

WHITELAW

The Development of Permanent
Colors for Estrich Plaster

Ceramic Engineering

B. S.

1915

THE UNIVERSITY
OF ILLINOIS
LIBRARY

1915
W587



THE DEVELOPMENT OF PERMANENT
COLORS FOR ESTRICH PLASTER

BY

JAMES CAMERON WHITELAW

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CERAMIC ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1915



Digitized by the Internet Archive
in 2013

<http://archive.org/details/developmentofper00whit>

1715
6587

UNIVERSITY OF ILLINOIS

May 31, 1905

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

James Cameron Whitelaw

ENTITLED THE DEVELOPMENT OF PERMANENT COLORS FOR ESTRICH

PLASTER

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Ceramic Engineering

Ralph K. Hersh

Instructor in Charge

APPROVED:

R. S. Still

HEAD OF DEPARTMENT OF Ceramics

1915

W537

TABLE OF CONTENTS

	Page
I INTRODUCTION	1
A Method of coloring	2
B Use of Alum in setting of plaster	2
II OUTLINE OF WORK	3
III METHOD OF COLORING	3
IV RESULTS.	
Series I Co - Al_2O_3 blue	4
Series II Cr - Sn Reds	5
Series III Cr - Sn Reds	6
Series IV Fe - Sb yellows	7
Series V Fe - Sb yellows	8
Series VI Blue by use of soda spar and CoSO_4	9
Series VII Nickel colors	10
Series VIII Effect of $\text{K}_2\text{Cr}_2\text{O}_7$ + CaCl_2	10
Series IX Effect of Fe_2O_3	10 - 11
Tensile strength and porosity of above samples.....	12
SUMMARY AND CONCLUSIONS	12

THE DEVELOPMENT OF PERMANENT

COLORS FOR ESTRICH PLASTER

INTRODUCTION

Estrich plaster is a slow setting Cement prepared by burning gypsum to temperatures somewhat above red heat. The product is not made in the United States, but is manufactured and sold to a considerable extent in Germany, chiefly as a flooring material.

It is made by burning either $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$, or $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, which has been finely ground, to a temperature above red heat. The cooled product is reground, and is then ready for use. After mixing with water to a mortar consistency it requires from 3 to 7 days to become fully hard. The set plaster compares with Portland cement in strength and hardness, is tough and resists weathering to a great extent.

Although estrich plaster is normally white it is often desirable to produce a colored mortar or cement. The method of coloring that has generally been used heretofore is by the use of aniline dyes, or other organic coloring compounds. This method of coloring has proved very unsatisfactory due to the fact that the organic coloring compounds are not permanent. They bleach, wash, and fade out, due to the chemical action of the sun's rays and the

basic Calcium hydroxide formed. Repeated washing also causes the colors to fade. Permanent colors are only obtainable with inorganic coloring agents, as frits, or colored compounds formed in the Cement itself.

The present study was intended to develop some satisfactory permanent colors in estrich plaster. On account of the extremely slow rate of setting of ordinary estrich plaster an alum solution was used to accelerate the hardening. This product is not a true estrich but resembles the Keene's, Mack's, or Scott's Cements used for wall-finish, artificial marble, etc. This alum cement is not as permanent as estrich plaster and will not withstand the weather but the effect of the colors is similar and the results obtained will be applicable to both products.

Bacher¹ found that the best method of permanently coloring estrich plaster was to grind the plaster (set plaster preferred), soak it in a soluble salt of the desired metal and calcine it at 1100°C.

By this method he was able to produce good uranium-yellow, manganese-brown, chromium-green, and fair cobalt-alumina blue colors. In my investigations I have attempted to produce a greater number of colors and also improve some of the ones that he developed.

1. Thesis for B. S. Degree in Ceramic Engineering, University of Illinois, by H. R. Bacher.

OUTLINE OF SCOPE OF INVESTIGATIONS

The method of producing colored cements in this work, has been limited entirely to the coloring of Estrich plaster by the soaking of the gypsum in a soluble metallic salt before calcining. It was shown by Bacher that this was the only practical method among the four he tried. The following divisions of the work were taken up:

- (1) Development of Cobalt-Aluminum blue.
- (2) Development of Iron-Antimony yellow.
- (3) Development of Chrome-tin pink.
- (4) Development of Blues by use of soda-spar and Cobalt.
- (5) Development of Nickel Colors.
- (6) Effect of adding $K_2Cr_2O_7 + CaCl_2$.
- (7) Effect of adding finely divided Fe_2O_3 to plaster and burning.
- (8) Tensile strength and porosity tests on samples of above plasters.

Throughout this work set plaster of paris was used as the body. Old molds and plaster casts were broken up and ground to pass 100 mesh. The correct amount of this plaster was weighed out, placed in a dish, mixed with the dry ingredients of the bodies and the coloring salts added in solution. The material was then thoroughly mixed, placed in an electric oven and dried at $110^{\circ}C$ for 5 hours. It was then ground to pass 100 mesh and screened several times to thoroughly mix it. Samples of 25 grams each were put in fire-clay assay crucibles and burned to about $1100^{\circ}C$.

After burning the product was again ground. In setting the sample was mixed with alum solution to a stiff paste, molded and placed in a moist chamber for a period of from 3 to 7 days.

SERIES I

COBALT ALUMINA BLUE.- The following mixtures of plaster, aluminum oxide, cobalt sulphate, and water glass were made, the Cobalt sulphate and water glass being added in solution.

A			B		
Plaster = 85%)	99%	-----	80%)
Al ₂ O ₃ = 15%)		-----	20%)
CaSO ₄ ----	1%		-----	1%	
C			D		
Plaster = 85%)	98%	-----	80%)
Al ₂ O ₃ = 15%)		-----	20%)
CaSO ₄ ----	1%		-----	1%	
Na ₂ Si ₄ O ₇ -	1%		-----	1%	

These were burned to 1110°C in 12 hours in a gas fired muffle kiln.

RESULTS

(A) and (B) were of a greenish-blue color and when mixed with H₂O and alum and allowed to set the material was soft and powdery. (C) was a good clear light blue, with no trace of green. When set it was of medium hardness. (D) was slightly darker than (C) and would make a good commercial color.

SERIES II

CHROME-TIN REDS.- The ratio of Chromium oxide to tin oxide in some of the best known Chrome-tin stains used in glazes, was made the basis of the following mixtures.

<u>A + C</u>		<u>B + D</u>
96.4%	----- Plaster -----	75.4%
2.0%	----- SnCl_2 -----	20.0%
1.6%	----- $\text{Cr}_2(\text{SO}_4)_3$ -----	4.6%

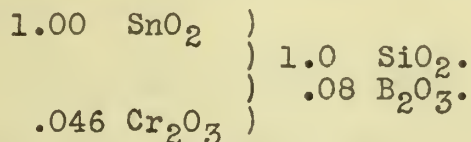
By mixing the plaster with a solution of alum before burning a product is obtained which sets more rapidly and produces a stranger body, as stated before. Since the presence of alum, however, might affect the color produced in using these materials, two mixtures, (IIC and IID), similar to II-A and II-B, were made into which alum was introduced by adding a 5% solution to the dry materials before burning.

The mixtures of series II were burned to 1075°C in 30 hours in a coal fired test kiln, and cooled slowly. Strong reducing conditions prevailed throughout the latter part of the burn. All the samples were of a light gray-green color. Thinking that the reducing conditions of the burn might have spoiled the colors the samples were reburned under oxidizing conditions to 1080°C . The resulting colors were practically the same as before. A good Chrome-tin red stain was observed around the inside of the crucible just above the sample, probably caused by some of the powder having stuck to the crucible, and developed the red color in burning due to its contact with Al_2O_3 and SiO_2 in the clay of the crucible.

The above results seem to indicate either that too much Chromium was present or that the presence of SiO_2 is necessary for the development of a Chrome-tin red color. Alumina does not seem to be necessary since there appeared to be no difference in the color of the mixtures which contained alum and those which did not.

SERIES III

In a further attempt to produce the red color a series of mixtures was made in which silica and borax were used. The proportions were taken from a red stain having the following formula:



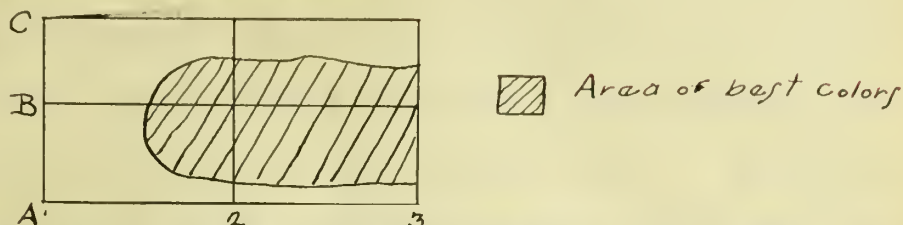
The mixtures were as follows:

	SnCl_2	Cr_2O_3	SiO_2	B_2O_3	Plaster
A ₁	2.0%	0.2%	1.0%	.15%	96.65%
A ₂	"	"	1.5%	"	Remainder
A ₃	"	"	2.0%	"	"
B ₁	"	"	1.0%	.25%	"
B ₂ ★	"	"	1.5%	"	"
B ₃	"	"	2.0%	"	"
C ₁	"	"	1.0%	.35%	"
C ₂	"	"	1.5%	"	"
C ₃	"	"	2.0%	"	"

★ Best.

The above group was burned to 1130°C in an open gas-fired kiln in 12 hours and cooled slowly.

Some very good red colors, almost of a rose-lilac shade, were developed, the best composition being that of B-2. The remainder were of a greenish-gray shade.



The best samples were mixed with alum and placed in a moist chamber to harden. The time required for initial set was 40 - 50 minutes and for a final set, about 3 days. At the end of this period they were very hard.

The results show that a good chrome-tin red can be produced but that SiO_2 and B_2O_3 are necessary for its development.

SERIES IV

IRON-ANTIMONY YELLOWS.- From formulas of yellow glazes which mature at 1050°C , using iron and antimony oxides as coloring agents the best ratio of these oxides seems to be .02 moles. of Fe_2O_3 to .08 moles. Sb_2O_3 or as 1 to 4. Accordingly the following mixtures were made introducing the iron and antimony compounds in this ratio.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Plaster -----	89.6%	89.1%	88.6%	88.1%
Sb_2O_3 -----	7.4%	7.4%	7.4%	7.4%
Fe SO_4 -----	3.0%	3.5%	4.0%	4.5%

Samples were made by adding the Sb_2O_3 , ground to pass 200 mesh, to the plaster and adding the proper amount of FeSO_4 in solution. Antimony oxide was used because there is no cheap antimony

salt. The mixtures were burned to 1070°C in a coal-fired kiln in 36 hours and cooled slowly.

Samples, mixed with alum had an initial set of 35 minutes and a final set of 2 days. The pieces developed a good degree of hardness. The colors varied from a light to a deep salmon-pink. All the samples contained spots of a good yellow color. The results seem to show that too much iron was present because (IV-D) was of a darker pink than (IV-A). They also show the possibilities of developing a good Fe-Sb yellow.

SERIES V

In this series the following mixtures were made, reducing the amount of FeSO_4 .

92.1 Plaster)		91.6 Plaster)	
7.4 Sb_2O_3)	V-A	7.4 Sb_2O_3)	V-B
0.5 FeSO_4)		1.0 FeSO_4)	
91.1 CaSO_4)		90.6 CaSO_4)	
7.4 Sb_2O_3)	V-C	7.4 Sb_2O_3)	V-D
1.5 FeSO_4)		2.0 FeSO_4)	

These were burned to 1075°C in an open fire gas kiln in 8 hours.

RESULTS

Numbers V-A and V-B were of a very good light yellow color while (V-C) and (V-D) showed to a considerable degree the salmon pink tinge. They set quickly with addition of alum and formed a hard plaster. The yellow color produced compares favorably with that obtained with uranium and is much cheaper. However, the dark

shades of yellow were not obtained by the use of iron and antimony.

SERIES VI

BLUE COLORS BY THE USE OF SODA-SPAR WITH COBALT SULPHATE.

In order to test the effect of soda-spar in bringing out the Cobalt blue color the following series was made:

97 Plaster)		95 Plaster)	
2 CoSO ₄)	VI-A	2 CoSO ₄)	VI-B
1 S. spar)		3 S. spar)	
93 CaSO ₄)		88 CaSO ₄)	
2 CoSO ₄)	VI-C	2 CoSO ₄)	VI-D
5 S. spar)		10 S. spar)	

The usual samples of 25 grams each were made and burned to 1070°C in a coal-fired kiln in 30 hours.

All of these were of a dirty gray-blue color. The sample after burning was hard and partially fused due to the fluxing action of the soda-spar.

Use of Soda-spar does not bring out a good cobalt blue color, those obtained being unsatisfactory for commercial use. The fluxing action of the feldspar causes the mixture to sinter, which would interfere with the grinding process.

SERIES VII

NICKEL COLORS.- The coloring effect of nickel salts was tried in the following mixtures, which were burned to 1070°C in a coal-fired kiln.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Plaster -----	99%	98%	97%	96%
NiSO ₄ -----	1%	2%	3%	4%

The colors obtained were of too dead a shade and did not possess enough brightness or life to be used to any great extent. They were all a bright greenish-gray shade of little or no commercial value. When mixed with alum the samples set to a fair degree of hardness.

SERIES VIII

In order to determine the coloring effect of additions of calcium chloride to potassium dichromate solutions of $K_2Cr_2O_7$ and $CaCl_2$ were mixed and added to ground plaster. The sample was burned to $1075^{\circ}C$ in an open fire gas kiln. A good yellow color having a slight tinge of green was produced.

SERIES IX

To determine the effect of adding finely divided Fe_2O_3 to the raw plaster and burning, two samples were made as follows: The Fe_2O_3 was ground to pass 200 mesh and the samples were burned to $1075^{\circ}C$ in an open fire gas-kiln.

24.7 Plaster)	IX-A	24.4 Plaster)	IX-B
(1%) 0.3 Fe_2O_3)		(2%) 6 Fe_2O_3)	

Sample (IX-A) was of fairly good red color while (IX-B) was a good deep red. The color was a somewhat dead shade which is typical of cement and mortar colors. When alum solution was added

to these mixtures a hard plaster was formed.

A good deep brick-red can be obtained by adding finely ground Fe_2O_3 to the raw plaster and burning.

A large quantity of the cobalt-alumina blue and the chrome-tin red plasters was made according to the best formulas obtained in the previous work.

2.00	SnCl_2)	
)	
.18	Cr O)	
)	
1.50	SiO_2)	$\text{Cr} - \text{Sn}$
)	
.25	B_2O_3)	
)	
96.07	Plaster)		

	2.00	CoSO_4)	
)	
	1.00	$\text{Na}_2\text{Si}_4\text{O}_9$)	
)	
(80.00	Plaster)		$\text{Co}-\text{Al}_2\text{O}_3.$
(
(20.00	Al_2O_3)	

97%

These batches were prepared as before, enough water added to make a stiff paste and the material molded into bricks. They were then burned to 1100°C in an open gas furnace in 8 hours. After burning the material was ground, screened, mixed with 5% alum solution and poured or pressed into standard tensile briquette molds. These were placed in a moist chamber and allowed to remain for 5 days at the end of this period the briquettes were tested for tensile strength and porosity.

The specimens showed an initial set in about one to one and one-half hours. After 7 days set in the moist chamber the tensile strength of the samples was as follows:

Co - Al_2O_3 Blue	(1. -----	375	Pounds per sq. in.
	(2. -----	360	"
	(3. -----	<u>310</u>	"
	Average		348 "

Cr - Sn Red	(4. -----	550	Pounds per sq. in.
	(5. -----	575	"
	(6. -----	<u>545</u>	"
	Average		557 "

The stronger body was also much the harder of the two.

The average porosity of the briquets was, for the Co - Al_2O_3 Blue body 1.41% and for the Cr - Sn Red body 1.03%. The lower strength and hardness of the blue body is undoubtedly due to the large content of Al_2O_3 which took no active part in the setting reaction. Another body of similar composition except for a lower percentage of Al_2O_3 developed much greater strength.

The briquets of the red body were very hard and smooth and the tensile strength compares well with that of portland cement.

SUMMARY AND CONCLUSIONS

A strong hard smooth cement with a wide range of good color may be produced by soaking ground, set gypsum plaster in soluble metallic salts and calcining the batch at 1100°C.

The following mixtures produced the best colors:

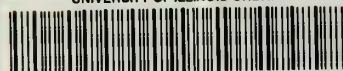
Cobalt - Alumina blue	(Plaster---80 %)	}----- 97 %
	(Al ₂ O ₃ ---20 %)	
	(CoSO ₄ -----	2 %
	(Na ₂ Si ₄ O ₉ -----	1 %
Chrome - tin Red	(SnCl ₂ -----	2.00 %
	(Cr ₂ O ₃ -----	.22 %
	(SiO ₂ -----	1.50 %
	(B ₂ O ₃ -----	.25 %
	(Plaster-----	96.03 %
Iron - Antimony yellow	(Plaster-----	91.85 %
	(Sb ₂ O ₃ -----	7.40 %
	(FeSO ₄ -----	.75 %

Using these colors, and some of those developed by Bacher, almost any desired tint may be obtained by blending.





UNIVERSITY OF ILLINOIS-URBANA



3 0112 079096548